

**PATENT APPLICATION**

**COLD-WORKED STEELS WITH  
PACKET-LATH MARTENSITE/AUSTENITE  
MICROSTRUCTURE**

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# COLD-WORKED STEELS WITH PACKET-LATH MARTENSITE/AUSTENITE MICROSTRUCTURE

## CROSS-REFERENCE TO RELATED APPLICATION

5 [0001] This patent application claims priority from United States Provisional Patent Application Serial No. 60/427,830, filed November 19, 2002, for all purposes legally capable of being served thereby. The contents of provisional patent application no. 60/427,830 are incorporated herein by reference in their entirety, as are all literature citations in this specification.

## 10 BACKGROUND OF THE INVENTION

### 1. Field of the Invention

[0002] This invention resides in the technology of low and medium carbon steel alloys, particularly those of high-strength and toughness, and the cold formability of such alloys.

### 2. Description of the Prior Art

15 [0003] An important step in the processing of high-performance steels is cold working, which typically consists of a series of compressions and/or expansions achieved by processes such as drawing, extruding, cold heading, or rolling. Cold working causes plastic deformation of the steel which produces strain hardening while forming the steel into the shape in which it will ultimately be used. Cold working, which in the case of steel wire is  
20 performed by wire drawing, is typically performed in a succession of stages with intermediate heat treatments, which in the case of steel wire are termed "patenting."

[0004] High-strength steel wire is an example of a high-performance steel and is useful in a variety of engineering applications including tire cord, wire rope, and strand for pre-stressed concrete reinforcements. The steel most commonly used in high-strength steel wire is  
25 medium- or high-carbon steel. In the typical procedure for forming the wire, hot-rolled rods with pearlitic microstructures are cold drawn in several stages, with intermediate patenting

treatments to soften the pearlite for continued cold drawing. For example, hot rolled rods of about 5.5 mm diameter might be coarse drawn in several stages to a diameter of about 3 mm. Patenting might then be performed at 850-900°C, causing austenitization of the steel, followed by transformation of the steel at 500-550°C to fine pearlitic lamellae. The steel would then be pickled, in hydrochloric acid, for example, to remove the scale formed during patenting. The pickling would be followed by several further drawing stages to reduce the diameter down to about 1 mm, then further patenting and pickling. The final drawing would then be done in several stages to the final desired diameter, which may for example be about 0.4 mm, to achieve the desired properties, notably strength. This may be followed by further processing such as stranding, depending on the ultimate use.

[0005] The purpose of the initial patenting treatment is to produce a wire rod with a fine lamellar pearlite structure, which requires a low transformation temperature. To achieve the desired temperature control, the process is typically performed in a molten lead bath. In the succeeding drawing stages, the wire is drawn to true strains (defined below) of 6-7 to obtain high strength levels of approximately 3,000 MPa. For conventional pearlitic wires, these high strains and strengths are attainable only by applying a series of patenting treatments. Without these patenting treatments, the cold drawing will cause shear cracking of the pearlitic lamellae. Because of the need for a molten lead bath the entire process is costly and tends to raise environmental concerns.

[0006] Cold working is also used in the production of expandable steel tubing, i.e., tubing that is expanded on-site and in some cases below ground.

[0007] A recent development in steel alloys is the formation of microstructures containing both martensite and austenite phases in an alternating configuration in which the martensite is present as laths that are separated by thin films of austenite. The microstructures are fused grains in which individual grains contain several laths of martensite separated by thin austenite films with, in some cases, an austenite shell surrounding each grain. These structures are termed “dislocated lath martensite” structures or “packet-lath” martensite/austenite” structures. Patents disclosing these microstructures are as follows, each of which is incorporated herein by reference in its entirety:

4,170,497 (Gareth Thomas and Bangaru V.N. Rao), issued October 9, 1979 on an application filed August 24, 1977

4,170,499 (Gareth Thomas and Bangaru V.N. Rao), issued October 9, 1979 on an application filed September 14, 1978 as a continuation-in-part of the above application filed on August 24, 1977

4,671,827 (Gareth Thomas, Nack J. Kim, and Ramamoorthy Ramesh), issued June 9, 1987 on an application filed on October 11, 1985

6,273,968 B1 (Gareth Thomas), issued August 14, 2001 on an application filed on March 28, 2000

While these microstructures offer certain performance benefits, notably a high resistance to corrosion, it has not heretofore been known that processing steps typically used for steel alloys could be simplified or eliminated when these microstructures are present.

**[0008]** Of further potential relevance to this invention are two United States patents that disclose the cold working of steel rods and wires without patenting. These patents are:

4,613,385 (Gareth Thomas and Alvin H. Nakagawa), issued September 23, 1986 on an application filed December 9, 1982

4,619,714 (Gareth Thomas, Jae-Hwan Ahn, and Nack-Joon Kim), issued October 28, 1986 on an application filed November 29, 1984 as a continuation-in-part of the above application filed on August 6, 1984

These patents are likewise incorporated herein in their entirety. The microstructures of the steels in these patents are considerably different from those of the first four patents listed above.

## SUMMARY OF THE INVENTION

**[0009]** It has now been discovered that the packet-lath martensite/austenite microstructure is unique in its crystallographic characteristics and how these characteristics cause it to respond to cold working. Because of the high dislocation density of this microstructure and the ease with which strains in the structure can move between the martensite and austenite phases, cold working provides the microstructure with unique mechanical properties that include a high tensile strength. As a result, these alloys can be cold worked without intermediate heat treatments, while still achieving tensile strengths comparable to the tensile strengths of conventional steel alloys that have been processed by cold working with intermediate heat treatments. In the case of steel wire having the packet-lath martensite/austenite microstructure, this invention lies in the discovery that cold drawing can

be performed without intermediate patenting treatments. In accordance with the present invention, therefore, carbon steel alloys having the packet-lath martensite/austenite microstructure, i.e., those whose microstructure includes laths of martensite alternating with thin films of retained austenite are cold formed, preferably without intermediate heat treatments, to a reduction sufficient to achieve a tensile strength of about 150 ksi or higher ("ksi" denotes kilo-pounds-force per square inch), equivalent to approximately 1,085 MPa or higher ("MPa" denotes megapascals, i.e., newtons per square millimeter). Cold working to tensile strengths of 2,000 MPa (290 ksi) or higher is of particular interest, and indeed, tensile strengths of 3,000 MPa (435 ksi) and as high as 4,000 MPa (580 ksi) can be achieved by the practice of this invention. These values are approximate; the conversion factor to the nearest thousandth is 6.895 MPa equal 1 ksi.

**[0010]** The benefits of this invention extend to simple packet-lath martensite/austenite microstructures containing no ferrite or insignificant amounts of ferrite, and also to microstructures that include packet-lath grains fused with ferrite grains, and to variants on these structures, including those whose packet-lath grains are encased by austenite shells, those that are free of interphase carbide precipitates, and those in which the austenite films are of a uniform orientation. The discovery of the ability of packet-lath martensite/austenite microstructures to respond to cold working in this manner is surprising relative to the disclosures in patents nos. 4,613,385 and 4,619,714 referenced above, since the ferrite in the microstructures of those patents has a lower yield strength than the martensite. As a result, the ferrite will preferentially absorb the strain introduced by the cold working, while the martensite will not respond to the cold working until the ferrite phase is work hardened to a level above the yield strength of the martensite. In the microstructures addressed by the present invention, the relatively low level of ferrite, or its absence when no ferrite is present, will cause the martensite to absorb the strain at an earlier stage of the cold working process. Martensite and ferrite are distinctly different from each other in crystal structure and hardening behavior.

**[0011]** These and other features, objects, advantages, and embodiments of the invention will be better understood from the descriptions that follow.

## BRIEF DESCRIPTION OF THE FIGURES

[0012] FIG. 1 is a plot of tensile strength vs. true total strain for two steel alloys of dual-phase packet-lath martensite/austenite microstructure, upon cold working in accordance with this invention in the absence of intermediate heat treatments.

- 5 [0013] FIG. 2 is a plot of tensile strength vs. true total strain for three steel alloys of triple-phase packet-lath martensite/austenite/ferrite microstructure and one steel alloy of dual-phase packet-lath martensite/austenite microstructure, upon cold working in accordance with this invention in the absence of intermediate heat treatments.

## DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

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[0014] Cold working in the practice of this invention can be performed by the use of techniques and equipment that have been used for cold working in the prior art on other steel alloys and microstructures. For alloys in the form of blooms, billets, bars, slabs or sheets, cold working may consist of rolling the steel between rollers or other means of compression to reduce the thickness of and elongate the steel. When cold working is performed by rolling, multiple reductions are achieved by multiple passes through a rolling mill. For rod-shaped or wire-shaped workpieces, cold working may consist of cold-drawing or extrusion through a die. For multiple reductions, the workpiece is extruded through a series of successively smaller dies. Tubing is achieved by drawing the steel through a ring-shaped die with a mandrel inside the die. For multiple passes, the tubing that has already been drawn is further drawn through a smaller ring-shaped die with a mandrel placed inside the tubing.

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[0015] Cold working is performed at a temperature below the lowest temperature at which recrystallization occurs. Suitable temperatures are therefore those that do not induce any phase change in the steel. For carbon steels, recrystallization typically occurs at approximately 1,000°C (1,832°F), and accordingly, cold working in accordance with this invention is performed well below this temperature. Preferably, cold working is performed at temperatures of about 500°C (932°F) or less, more preferably about 100°C (212°F) or less, and most preferably at a temperature that is within about 25°C of ambient temperature.

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[0016] Cold working can be performed in a single pass or in a succession of passes. In either case, intermediate heat treatments (which, in the case of steel wire, are termed “patenting”) may be performed for further improvement in properties, but the properties resulting from the cold working alone are sufficiently high that the intermediate heat

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treatments are not required and are preferably not performed. The degree of reduction per pass is not critical to the invention and can vary widely, although the reductions should be great enough to avoid hardening the steel so much that the steel becomes susceptible to breakage after a small total reduction. In most cases, preferred reductions are at least about 20% per pass, more preferably at least about 25% per pass, and most preferably from about 25% to about 50% per pass. The reduction per pass is at least partially governed by such factors as the die angle and the drawing efficiency coefficient. The larger the die angle, the larger the minimum reduction that is required to avoid central burst cracking. The lower the drawing efficiency coefficient, however, the lower the maximum reduction for a steel with a given strain hardening exponent. A compromise is typically sought between these two competing considerations. In terms of the tensile strength of the final product, the cold working will preferably be performed to a tensile strength within the range of from about 150 ksi to about 500 ksi.

[0017] The process of this invention is applicable to carbon steel alloys having packet-lath martensite/austenite microstructures such as those described in the patents cited above, as well as those described in co-pending United States Patent Applications Nos. 10/017,847, filed December 15, 2001 (entitled "Triple-Phase Nano-Composite Steels," inventors Kusinski, G.J., Pollack, D., and Thomas, G.), and 10/017,879, filed December 14, 2001 (entitled "Nano-Composite Martensitic Steels," inventors Kusinski, G.J., Pollack, D., and Thomas, G.), both of which are incorporated herein by reference in their entirety. To permit formation of the packet-lath martensite/austenite microstructure, the alloy composition will typically have a martensite start temperature  $M_s$  of about 300°C or higher, and preferably 350°C or higher. While alloying elements in general affect the  $M_s$ , the alloying element that has the strongest influence on the  $M_s$  is carbon, and achieving an alloy with  $M_s$  above 300°C can be achieved by limiting the carbon content of the alloy to a maximum of 0.35% by weight. In preferred embodiments of the invention, the carbon content is within the range of from about 0.03% to about 0.35%, and in more preferred embodiments, the range is from about 0.05% to about 0.33%, all by weight. Further alloying elements, such as molybdenum, titanium, niobium, and aluminum, can also be present in amounts sufficient to serve as nucleation sites for fine grain formation yet low enough in concentration to avoid affecting the properties of the finished alloy by their presence. The concentration should also be low enough to avoid the formation of inclusions and other large precipitates, which may render the steel susceptible to early fracture. In certain embodiments of the invention, it will be

advantageous to include one or more austenite stabilizing elements, examples of which are nitrogen, manganese, nickel, copper, and zinc. Particularly preferred among these are manganese and nickel. When nickel is present, the nickel concentration is preferably within the range of about 0.25% to about 5%, and when manganese is present, the manganese concentration is preferably within the range of from about 0.25% to about 6%. Chromium is also included in many embodiments of the invention, and when it is present, the chromium concentration is preferably from about 0.5% to about 12%. All concentrations herein are by weight.

**[0018]** Certain embodiments of the invention involve alloys that include a ferrite phase in addition to the packet-lath martensite/austenite grains (triple-phase alloys) while others contain only the packet-lath martensite/austenite grains and do not include a ferrite phase (dual-phase alloys). In general, the presence or absence of the ferrite phase is determined by the type of heat treatment in the initial austenitization stage. By appropriate selection of the temperature, the steel can be transformed into a single austenite phase or into a two-phase structure containing both austenite and ferrite. In addition, the alloy composition can be selected or adjusted to either cause ferrite formation during the initial cooling of the alloy from the austenite phase or to avoid ferrite formation during the cooling, i.e., to avoid the formation of ferrite grains prior to the further cooling of the austenite to form the packet-lath microstructure.

**[0019]** As noted above, in certain cases it will be beneficial to use alloys with packet-lath martensite/austenite microstructures in which the austenite films in a single packet-lath grain are all of approximately the same orientation, although the crystallographic orientation may vary, or those in which the austenite films in a single packet-lath grain are all of the same crystal plane orientation. The latter can be achieved by limiting the grain size to ten microns or less. Preferably, the grain size in these cases is within the range of about 1 micron to about 10 microns, and most preferably from about 5 microns to about 9 microns.

**[0020]** The preparation of -phase packet-lath martensite/austenite microstructures that do not contain ferrite (i.e., "dual-phase" microstructures) begins with the selection of the alloy components and the combining of these components in the appropriate portions as indicated above. The combined components are then homogenized ("soaked") for a sufficient period of time and at a sufficient temperature to achieve a uniform austenitic structure with all elements and components in solid solution. The temperature will be above the austenite recrystallization temperature but preferably at a level that will cause very fine grains to form. The austenite recrystallization temperature typically varies with the alloy composition, but in



general will be readily apparent to those skilled in the art. In most cases, best results will be achieved by soaking at a temperature within the range of 800°C to 1150°C. Rolling, forging or both are optionally performed on the alloy at this temperature.

**[0021]** Once homogenization is completed, the alloy is subjected to a combination of

5 cooling and grain refinement to the desired grain size, which as noted above may vary. Grain refinement may be performed in stages, but the final grain refinement is generally achieved at an intermediate temperature that is above, yet close to, the austenite recrystallization temperature. The alloy may first be rolled at the homogenization temperature to achieve dynamic recrystallization, then cooled to an intermediate temperature and rolled again for  
10 further dynamic recrystallization. The intermediate temperature is between the austenite recrystallization temperature and a temperature that is about 50 degrees Celsius above the austenite recrystallization temperature. For alloy compositions whose austenite recrystallization temperature is about 900°C, and the intermediate temperature to which the alloy is cooled is preferably between about 900° to about 950°C, and most preferably  
15 between about 900° to about 925°C. For alloy compositions whose austenite recrystallization temperature is about 820°C, the preferred intermediate temperature is about 850°C. Dynamic recrystallization can also be achieved by forging or by other means known to those skilled in the art. Dynamic recrystallization produces a grain size reduction of 10% or greater, and in many cases a grain size reduction of from about 30% to about 90%.

20 **[0022]** Once the desired grain size is achieved, the alloy is quenched by cooling from a temperature above the austenite recrystallization temperature down to the martensite start temperature  $M_s$ , then through the martensite transition range to convert the austenite crystals to the packet-lath martensite/austenite microstructure. When ferrite crystals are present among the austenite crystals, the conversion occurs only in the austenite crystals. The  
25 optimal cooling rate varies with the chemical composition, and hence the hardenability, of the alloy. The resulting packets are of approximately the same small size as the austenite grains produced during the rolling stages, but the only austenite remaining in these grains is in the thin films and in some cases in the shell surrounding each packet-lath grain. When the thin austenite films are to be of a single variant in crystal orientation, this is achieved by  
30 controlling the process to achieve a grain size of less than 50 microns.

**[0023]** As an alternative to dynamic recrystallization, grain refinement to the desired grain size can be accomplished by heat treatment alone. To use this method, the alloy is quenched as described in the preceding paragraph, then reheated to a temperature that is approximately

equal to the austenite recrystallization temperature or slightly below, then quenched once again to achieve, or to return to, the packet-lath martensite/austenite microstructure. The reheating temperature is preferably within about 50 degrees Celsius of the austenite recrystallization temperature, for example about 870°C.

5 **[0024]** Processing steps such as heating the alloy composition to the austenite phase, cooling the alloy with controlled rolling or forging to achieve the desired reduction and grain size, and quenching the austenite grains through the martensite transition region to achieve the packet-lath structure are performed by methods known in the art. These methods include castings, heat treatment, and hot working of the alloy such as by forging or rolling, followed  
10 by finishing at the controlled temperature for optimum grain refinement. Controlled rolling serves various functions, including aiding in the diffusion of the alloying elements to form a homogeneous austenite crystalline phase and in the storage of strain energy in the grains. In the quenching stages of the process, controlled rolling guides the newly forming martensite phase into a packet-lath arrangement of martensite laths separated by thin films of retained  
15 austenite. The degree of rolling reduction can vary and will be readily apparent to those of skill in the art. Quenching is preferably done fast enough to avoid formation of detrimental microstructures including pearlite, bainite, and particles or precipitates, particularly interphase precipitation and particle formation, including the formation of undesirable carbides and carbonitrides. In the packet-lath martensite-austenite grains, the retained  
20 austenite films will constitute from about 0.5% to about 15% by volume of the microstructure, preferably from about 3% to about 10%, and most preferably a maximum of about 5%.

**[0025]** Triple-phase alloys have a microstructure consisting of two types of grains, ferrite grains and packet-lath martensite/austenite grains, fused together as a continuous mass. As in  
25 the dual-phase alloys, the individual grain size is not critical and can vary widely. For best results, the grain sizes will generally have diameters (or other appropriately characteristic linear dimension) that fall within the range of about 2 microns to about 100 microns, or preferably within the range of about 5 microns to about 30 microns. The amount of ferrite phase relative to the martensite-austenite phase may vary. In most cases, however, best  
30 results will be obtained when the martensite/austenite grains constitute from about 5% to about 95% of the triple-phase structure, preferably from about 15% to about 60%, and most preferably from about 20% to about 40%, all by weight.

**[0026]** Triple-phase alloys can be prepared by first combining the appropriate components needed to form an alloy of the desired composition, then soaking to achieve a uniform

austenitic structure with all elements and components in solid solution, as in the preparation of the dual-phase alloys described above. A preferred soaking temperature range is from about 900°C to about 1,170°C. Once the austenite phase is formed, the alloy composition is cooled to a temperature in the intercritical region, which is defined as the region in which austenite and ferrite phases coexist at equilibrium. The cooling thus causes a portion of the austenite to transform into ferrite grains, leaving the remainder as austenite. The relative amounts of each of the two phases at equilibrium varies with the temperature to which the composition is cooled in this stage, and also with the levels of the alloying elements. The distribution of the carbon between the two phases (again at equilibrium) also varies with the temperature. The relative amounts of the two phases are not critical to the invention and can vary. The temperature to which the composition is cooled in order to achieve the dual-phase ferrite-austenite structure is preferably within the range of from about 800°C to about 1,000°C.

[0027] Once the ferrite and austenite crystals are formed (i.e., once equilibrium at the selected temperature in the intercritical phase is achieved), the alloy is rapidly quenched by cooling through the martensite transition range to convert the austenite crystals to the packet-lath martensite/austenite microstructure. The cooling rate used during this transition is great enough to substantially avoid any changes to the ferrite phase and to avoid undesirable austenite decomposition. Depending on the alloy composition and its hardenability, water cooling may be required to achieve the desired cooling rate, although for certain alloys air cooling will suffice. In some alloys, notably triple-phase containing 6% Cr, the desired cooling rate is slow enough that air cooling can be used. The considerations noted above in connection with dual-phase alloys apply here as well.

[0028] Preferred dual-phase alloy compositions are those that contain from about 0.04% to about 0.12% carbon, from zero to about 11.0% chromium, from zero to about 2.0% manganese, and from zero to about 2.0% silicon, all by weight, the remainder being iron. Preferred triple-phase alloy compositions are those that contain from about 0.02% to about 0.14% carbon, from zero to about 3.0% silicon, from zero to about 1.5% manganese, and from zero to about 1.5% aluminum, all by weight, the remainder being iron.

[0029] The formation of precipitates or other small particles within the microstructure upon cooling is collectively referred to as “autotempering.” In certain applications of this invention, whether dual-phase or triple-phase alloys, autotempering will purposely be avoided by using a relatively fast cooling rate. The minimum cooling rates that will avoid

autotempering are evident from the transformation-temperature-time diagram for the alloy. In the typical diagram, the vertical axis represents temperature and the horizontal axis represents time, while curves on the diagram indicate the regions where each phase exists either by itself or in combination with another phase(s). A typical such diagram is shown in  
5 Thomas, U.S. Patent No. 6,273,968 B1, referenced above. In such diagrams, the minimum cooling rate is a line of descending temperature over time which abuts the left side of a C-shaped curve. The region to the right of the curve represents the presence of carbides, and cooling rates that avoid carbide formation are therefore those represented by lines that remain to the left of the curve. The line that is tangential to the curve has the smallest slope and is  
10 therefore the slowest rate that can be used while still avoiding carbide formation.

**[0030]** The terms “interphase precipitation” and “interphase precipitates” are used herein to denote the formation of small alloy particles at locations between the martensite and austenite phases, i.e., between the laths and the thin films separating the laths. “Interphase precipitates” does not refer to the austenite films themselves. Interphase precipitates are to be  
15 distinguished from “intrapphase precipitates,” which are precipitates located within the martensite laths rather than along the interfaces between the martensite laths and the austenite films. Intrapphase precipitates that are about 500Å or less in diameter are not detrimental to toughness and may in fact enhance toughness. Thus, autotempering is not necessarily detrimental provided that the autotempering is limited to intrapphase precipitation and does not  
20 result in interphase precipitation. The term “substantially no carbides” is used herein to indicate that if any carbides are present, their distribution and amount are such that they have a negligible effect on the performance characteristics, and particularly the corrosion characteristics, of the finished alloy.

**[0031]** Depending on the alloy composition, a cooling rate that is sufficiently high to  
25 prevent carbide formation or autotempering in general may be one that can be achieved with air cooling or one that requires water cooling. In alloy compositions in which autotempering can be avoided with air cooling, air cooling can still be done when the levels of certain alloying elements are reduced provided that the levels of other alloying elements are raised. For example, a reduction in the amount of carbon, chromium, or silicon can be compensated  
30 for by raising the level of manganese.

**[0032]** The processes and conditions set forth in the U.S. patents referenced above, particularly heat treatments, grain refinements, on-line forgings and the use of rolling mills for rounds, flats, and other shapes, may be used in the practice of the present invention for the heating of the alloy composition to the austenite phase, the cooling of the alloy from the

austenite phase to the intercritical phase in the case of triple-phase alloys, and then the cooling through the martensite transition region. Rolling is performed in a controlled manner at one or more stages during the austenitization and first-stage cooling procedures, for example, to aid in the diffusion of the alloying elements to form a homogeneous austenite crystalline phase and then to deform the crystal grains and store strain energy in the grains, while in the second-stage cooling, rolling can serve to guide the newly forming martensite phase into the packet-lath arrangement of martensite laths separated by thin films of retained austenite. The degree of rolling reductions can vary, and will be readily apparent to those skilled in the art. In the packet-lath martensite-austenite crystals, the retained austenite films will constitute from about 0.5% to about 15% by volume of the microstructure, preferably from about 3% to about 10%, and most preferably a maximum of about 5%. The proportion of austenite relative to the entire triple-phase microstructure will be a maximum of about 5%. The actual width of a single retained austenite film is preferably within the range of about 50Å to about 250Å, and preferably about 100Å. The proportion of austenite relative to the entire triple-phase microstructure will in general be a maximum of about 5%. The rolling discussed in this paragraph is to be distinguished from the cold working that is done in accordance with this invention after the packet-lath martensite/austenite microstructures, whether dual-phase or part of a triple-phase structure, have been formed.

[0033] The following examples are offered only by way of illustration.

## EXAMPLE 1

[0034] This example illustrates the deformation of a carbon steel rod with a packet-lath martensite/austenite microstructure, by a cold drawing process according to the present invention to an area reduction of 99%.

[0035] The experiment reported in this example was performed on a steel rod measuring 6 mm in diameter and having an alloy composition of 0.1% carbon, 2.0% silicon, 0.5% chromium, 0.5% manganese, all by weight, and the balance iron, with a microstructure consisting of grains measuring approximately 50 microns in diameter, each grain consisting of laths of martensite measuring approximately 100 nm in thickness alternating with thin films of austenite measuring approximately 10 nm in thickness, with no ferrite phases and each grain surrounded by an austenite shell measuring approximately 10 nm in thickness.

The rod was prepared by the method described in co-pending United States patent application serial no. 10/017,879, filed December 14, 2001, referenced above.

[0036] The uncoated steel rod was surface cleaned and lubricated, then cold drawn through lubricated dies in 15 passes at a temperature of 25°C to a diameter of 0.0095 inch (0.024 cm).

5 At a final wire diameter of 0.0105 inch (0.027 cm), representing a total area reduction of 99%, the wire had a tensile strength of 390 ksi (2,690 MPa).

## EXAMPLE 2

[0037] This example is another illustration of the cold working of carbon steel rods with packet-lath martensite/austenite microstructures in accordance with the present invention. In

10 this example, two different alloys were used, Fe/8Cr/0.05C and Fe/2Si/0.1C, with a microstructure consisting of grains measuring approximately 50 microns in diameter, each grain consisting of laths of martensite measuring approximately 150 nm in thickness alternating with thin films of austenite measuring approximately 10 nm in thickness, with no significant ferrite phases, each grain surrounded by an austenite shell measuring

15 approximately 10 nm in thickness.

[0038] The steel rods were 6 mm in diameter, and were surface cleaned and lubricated, then cold drawn through lubricated dies in a series of passes at a temperature of 25°C. The drawing schedule shown in Table I was used for the Fe/8Cr/0.05C alloy, and a similar drawing schedule was used for the Fe/2Si/0.1C alloy. In this table,  $A_0$  represents the initial

20 rod diameter and  $A$  is the rod diameter after the particular pass.

**TABLE I**  
**Drawing Schedule for Fe/8Cr/0.05C With Substantially**  
**Ferrite-Free Packet-Lath Martensite Microstructure**

Pass No.	Diameter (mm)	True Total Strain ( $\ln(A/A_0)$ )	Single Pass Area Reduction (%)	Total Area Reduction (%)
(initial)	6.000	0.0	0.0	0.0
1	4.3	0.7	48.2	48.2
2	3.4	1.1	37.0	67.3
3	2.7	1.6	37.1	79.4
4	2.2	2.0	34.0	86.4
5	1.8	2.5	36.6	91.4
6	1.4	2.9	38.5	94.7
7	1.0	3.5	45.4	97.1

**[0039]** Tensile strengths were measured on the starting rod and after each pass, and the results are plotted against the true total strain in FIG. 1, in which the squares represent the Fe/8Cr/0.05C alloy and the diamonds represent the Fe/2Si/0.1C alloy. The Figure shows that the tensile strengths of both alloys reach approximately 2,000 MPa by the end of the entire drawing sequence at a total area reduction of 97%.

### EXAMPLE 3

**[0040]** This example illustrates cold working in accordance with the present invention, using carbon steel rods with packet-lath martensite/austenite microstructures that contain ferrite crystals as a third phase (in addition to the laths of martensite and the thin films of austenite, i.e., a triple-phase microstructure).

**[0041]** In this example, the alloy was Fe/2Si/0.1C, with a microstructure consisting of ferrite fused with packet-lath grains similar to those described above in Examples 1 and 2, containing martensite laths alternating with thin films of austenite and encased in an austenite shell. The rods were prepared by the method described in United States patent application no. 10/017,847, filed December 14, 2001, referenced above, using a reheat temperature of 950°C to achieve a ferrite content of 70 volume percent of the microstructure. The initial rod

diameter was 0.220 inch (5.59 mm), and the cold working consisted of drawing the rods through lubricated conical dies at a temperature of 25°C in 15 passes with approximately 36% reduction per pass to a final diameter of 0.037 inch (0.94 mm).

- 5 [0042] The drawing schedule is shown in Table II, where  $A_0$  represents the initial rod diameter and  $A$  is the rod diameter after the particular pass.

TABLE II  
Drawing Schedule for Fe/2Cr/0.1C With  
Triple-Phase Microstructure

Pass No.	Diameter (mm)	True Total Strain ( $\ln(A/A_0)$ )	Single Pass Area Reduction (%)	Total Area Reduction (%)
(initial)	6.050	0.00	0.00	0.00
1	4.580	0.56	42.69	42.69
2	3.650	1.01	36.49	63.60
3	2.910	1.46	36.44	76.86
4	2.320	1.92	36.44	85.29
5	1.870	2.35	35.03	90.45
6	1.660	2.59	21.20	92.47
7	1.320	3.04	36.77	95.24
8	1.090	3.43	31.81	96.75
9	0.910	3.79	30.30	97.74
10	0.756	4.16	30.98	98.44
11	0.624	4.54	31.87	98.94
12	0.526	4.89	28.94	99.24
13	0.437	5.26	30.98	99.48
14	0.390	5.48	20.35	99.58
15	0.359	5.65	15.27	99.65

- [0043] The tensile strength of the final wire was 2760 MPa (400 ksi).



#### EXAMPLE 4

[0044] This example is a further illustration of the cold work of carbon steel rods whose microstructure consists of packet-lath martensite/austenite and ferrite crystals, in accordance with the present invention.

5 [0045] In this example, the alloy was Fe/2Si/0.1C as in Example 3, with a microstructure consisting of ferrite fused with packet-lath grains similar to those described above in Examples 1 and 2, containing martensite laths alternating with thin films of austenite and encased in an austenite shell. A rod of this composition was prepared by the general method described in United States patent application no. 10/017,847, filed December 14, 2001,  
10 referenced above. In this case, the rod was initially hot rolled to a diameter of 0.25 inch (6.35 mm), then heated to 1,150°C for about 30 minutes to austenitize the composition, then quenched in iced brine to transform the austenite to substantially 100% martensite, then rapidly reheated to convert the structure to approximately 70% ferrite and 30% austenite. The rod was then quenched in iced brine to convert the austenite to the packet-lath  
15 martensite/austenite structure. The rod was then cold drawn in 7 passes at a reduction of 35% per pass to a final diameter of 0.055 inch (1.40 mm), resulting in a tensile strength of 1,875 MPa (272 ksi). In a parallel experiment, a rod of the same composition and treated in the identical manner was cold drawn in 13 passes at a reduction of 35% per pass to a final diameter of 0.015 inch (0.37 mm), resulting in a tensile strength of 2,480 MPa (360 ksi).

#### EXAMPLE 5

20 [0046] This example is a still further illustration of the cold working of carbon steel rods whose microstructure consists of packet-lath martensite/austenite and ferrite crystals, in accordance with the present invention, demonstrating the effect of varying the relative amounts of packet-lath martensite/austenite and ferrite.

25 [0047] The steel alloy was Fe/2Si/0.1C as in Examples 3 and 4, and the rods were prepared as described in Example 4, using different reheat temperatures to achieve ferrite contents of 0%, 56%, 66%, and 75%, corresponding to contents of packet-lath martensite/austenite contents of 100%, 44%, 35%, and 25%, respectively, all by volume. Drawing schedules similar to that shown in Table II were used on all four microstructures, and the resulting  
30 tensile strengths are plotted against the true total strain in FIG. 2, in which the squares represent the 100% packet-lath alloy, the triangles represent the 44% packet-lath alloy, the

circles represent the 34% packet-lath alloy, and the diamonds represent the 25% packet-lath alloy. The plot shows that all four microstructures achieved a tensile strength well in excess of 2,000 MPa, and those in which the packet-lath martensite/austenite portions exceeded 25% produced higher tensile strengths than the microstructure in which the packet-lath portion was 25%.

**[0048]** The foregoing is offered primarily for purposes of illustration. Further modifications and variations of the various parameters of the alloy composition and the processing procedures and conditions may be made that still embody the basic and novel concepts of this invention. These will readily occur to those skilled in the art and are included within the scope of this invention.